

Interface Reactions During Oxygen Plasma Assisted Chemical Vapor Deposition of Yttrium Oxide on Silicon

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Introduction

The continuous scaling of complementary metal-oxide-semiconductor (CMOS) devices requires an equivalent of a sub-1 nm silicon dioxide for gate dielectrics. Several metal oxides, including Al_2O_3 , Y_2O_3 , La_2O_3 , HfO_2 , and ZrO_2 that are potentially stable in contact with silicon, have been under investigation to replace SiO_2 . Several research groups have reported results that demonstrate oxidation of the silicon substrate during deposition or during post-deposition anneals. Understanding and controlling interface and bulk chemical stability of chemical vapor deposition (CVD) high-k dielectrics has become an important research issue. In this paper, we report thin Y_2O_3 films deposited by oxygen plasma assisted CVD using two yttrium diketonate precursors, and the relation between the precursor structure and the film properties is discussed. Interface and bulk properties and reaction mechanisms are addressed.

Experimental

A remote plasma CVD reactor was used in this study. It allows gas flow into a top plasma excitation region, and metal-organic precursor inlet downstream through a tube, with the tube outlet positioned close to the silicon substrate. Two solid metal organic precursors were utilized: yttrium hexafluoroacetylacetonate ($\text{Y}(\text{HFAA})_3$), and tris(2,2,6,6-tetramethyl-3,5-heptanedionato)yttrium ($\text{Y}(\text{TMHD})_3$).

Thin films ($<100 \text{ \AA}$) were analyzed using X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and electron energy loss spectroscopy (EELS). Relatively thick films ($\sim 500 \text{ \AA}$) were analyzed using Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), and Atomic Force Microscope (AFM). Capacitance-voltage (C-V) and current-voltage (I-V) measurements were conducted on MOS capacitors.

Results and Discussion

Figure 1 shows the XPS spectra of the Y 3d region for films deposited at 400°C for 3, 6.5, and 30 minutes using $\text{Y}(\text{TMHD})_3$. After deposition, films were annealed *ex-situ* at 900°C in N_2 ambient for 1 minute. The thickest film shows features consistent with Y_2O_3 structure in the Y 3d at $156.8 (3d_{5/2})$. O 1s and Si 2p spectra are also consistent with a thick Y_2O_3 film. The spectra for the film deposited for 3 minutes show significant shifts in Y 3d and O 1s binding energy, consistent with an oxide structure that contains significant Y-O-Si (Y-silicate) bonding. Figure 2 shows STEM/EELS results of the same 3-minute deposition film as in Figure 1. The TEM image in 2(a) shows the fine structure of the silicate film with thickness of 65 \AA . A close look with the annual dark-field (ADF) detector (inset of 2b) indicates that the film composition changes across the film. Figure 2(b) shows the Si L-edge electron energy loss spectrum measured at different locations across the film. Region 1 is the silicon substrate with an energy loss of 102 eV and clear periodic fringes shown by TEM. In region 2, the peak shifts to a higher energy loss

(109 eV) and yttrium concentration is below the detection limit of the instrument (~ 10 atomic percent for yttrium), which is consistent with a more SiO_2 -like structure, with possibly some Y incorporation. Region 3 shows a lighter contrast in the ADF image as compared to region 2, and the Si L-edge peak shifts slightly from 109 eV to a lower energy loss of 108.7 eV . Another feature at 116 eV also becomes more distinct. These spectral signatures clearly indicate a more yttrium-rich structure mixed with Si-O in region 3 of this film.

The data presented above shows that during plasma assisted CVD of Y_2O_3 based dielectrics, the initial deposited layers will mix and react with the substrate silicon to form a thin metal silicate or silicon oxide interface structure. Further deposition results in a film with composition closer to Y_2O_3 . Pre-nitridation of the silicon surface impedes the reaction with the substrate, promoting the Y_2O_3 structure. More XPS, TEM/EELS, FTIR, XRD, AFM, C-V, I-V results, and several possible mechanisms consistent with the observed results, including Si diffusion and reaction with absorbed OH, will be presented and discussed.

Acknowledgement

The authors thank the funding from SRC/SEMATECH Center for Front End Processes and NSF Grant CTS-0072784.

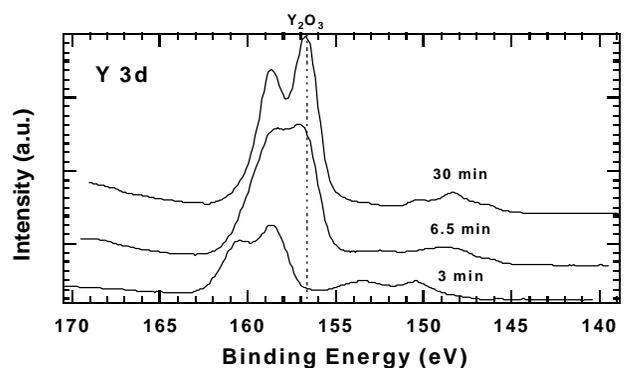


Figure 1. XPS results of films with different thicknesses from hydrogenated precursor $\text{Y}(\text{TMHD})_3$.

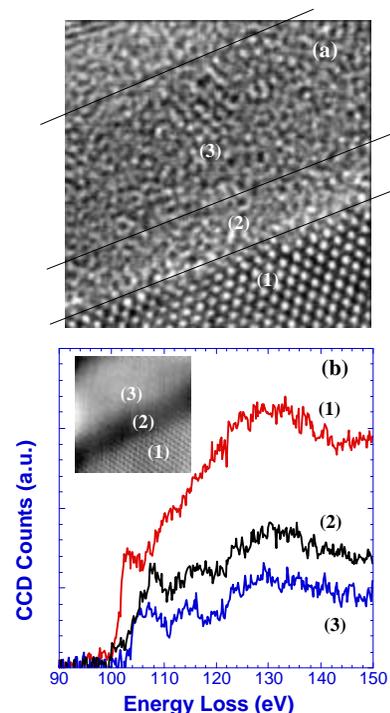


Figure 2. (a) TEM of the film deposited at 400°C for 3 min and annealed at 900°C for 1 min. The thickness is about 65 \AA ; (b) Si L-edges measured across the film. The locations correspond to those on the TEM image.